A CRITICAL EXPERIMENTAL STUDY OF THE HYDRATION AND REACTIVITY OF OXIDES

BY

ROBERT STEACY SPRAGUE

B.S., Washington and Jefferson College, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

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A CRITICAL EXPERIMENTAL STUDY OF THE HYDRATION AND REACTIVITY OF OXIDES

Introduction

This thesis is concerned with the behavior of two very common oxides, CaO and MgO, as they occur in the calcinate of a dolomitic limestone. The application of x-ray and electron microscopy techniques in recent years, particularly at the University of Illinois (1,2,3,4), has shed considerable light on the problems of the lime industry. Due to the presence of the less basic MgO, the problems of the dolomitic lime industry are more complex than those of the high calcium branch. In the last 12 years, the claim (5,6) has been made that ordinary dolomitic hydrated lime (containing essentially $Ca(OH)_2$ and MgO) is an unsound material for use in plasters and finishing coats because the MgO will slowly hydrate on the wall and cause expansion and physical failure. The method used to verify this theory is somewhat questionable and furthermore, extensive x-ray and thermal analysis studies (4) at the University of Illinois failed to substantiate this idea. This research was therefore undertaken to throw further light on the aging processes undergone by dolomitic limes and dolomitic hydrates with respect to the compounds formed and to assess the worth of the various analytical methods used to determine these compounds.

Experimental And Discussion

The Norelco Geiger-Muller X-ray Spectrometer was used extensively in this work to prepare easily interpreted powder diffraction patterns in a relatively short period of time. The Norelco instrument was shown to be as sensitive as the film technique in the detection of constituents present to the extent of 1-5% in these lime samples, provided that the sample particle size is correct and that the instrument is correctly adjusted and operated. The method of differential thermal

analysis, as described by Grim and Rowland (7), was used to detect compounds that undergo thermal decomposition somewhere between 100° and 1000° C. and thus to check the x-ray findings. Loss on ignition and on CO_2 analyses were carried out parallel with the x-ray method to determine the total water and carbon dioxide contents.

Dry, powdered CaO, $Ca(OH)_2$, MgO, and $Mg(OH)_2$ were found to be unreactive toward dry CO_2, but CaO and $Ca(OH)_2$ were readily converted to $CaCO_3$ by CO_2 saturated with water vapor. $Mg(OH)_2$ reacts with wet CO_2 to form $MgCO_3 \cdot 3H_2O$ as the main product with smaller amounts of $MgCO_3$. MgO, of ordinary density and calcined at 900° C. for 1 hour, reacts to a slight extent with wet CO_2 to form $MgCO_3 \cdot 3H_2O$, but the bulk of the water and CO_2 taken up was shown to be uncombined. MgO, when prepared from a light, porous basic carbonate by calcination at the minimum decomposition temperature, showed a greater tendency to hydrate when treated with water vapor than did the oxide calcined at higher temperature, but still tended to take up some water in an uncombined or "zeolitic" manner.

Soaking of normal dolomitic hydrate in water will hydrate the MgO in amounts depending on the time of soaking, but treatment of the dry, powdered normal dolomitic hydrate with water vapor causes only a very slight increase in $Mg(OH)_2$ content. If excess CO_2 is present with the water vapor, some $MgCO_3 \cdot 3H_2O$ is formed, even in the presence of $Ca(OH)_2$, and, of course, some $Ca(OH)_2$ is converted to $CaCO_3$. Soaking of plaster pats, made of dolomitic lime or hydrate and gauged with plaster of Paris or sand, in carbonated water will hydrate considerable quantities of MgO without producing expansion and physical failure.

Extensive work has shown that no chemical or thermochemical method (which depends on the loss on ignition at various temperatures to determine the amounts of thermally decomposable compounds present) is capable of accurately determining the percentage of $Mg(OH)_2$ and other compounds

present due to the tendency of these materials to take up firmly-held uncombined water which cannot be thermally distinguished from water of constitution, the uncertainty as to how the CO_2 is combined with the MgO (whether as $MgCO_3 \cdot 3H_2O$ or $MgCO_3$ or both), and the fact that the thermal decomposition regions of $Ca(OH)_2$, $Mg(OH)_2$, and $MgCO_3 \cdot 3H_2O$ overlap sufficiently so that accurate determinations of these compounds by a thermochemical procedure is impossible.

The marked decrease in reactivity exhibited by MgO as the calcination temperature is increased is explained on the basis of particle size increase and lattice perfection of the crystallites which enhances the more weakly basic character of magnesium. MgO exhibits a small degree of hydrous oxide character in its reaction toward water and it is probable that all magnesium hydroxide preparations contain several percent of $MgO \cdot xH_2O$.

Summary

The aging reactions of a dolomitic lime under atmospheric conditions have been shown to be complicated by the fact that water and possibly also CO_2 is taken up and held firmly in an uncombined manner and that $Mg(OH)_2$ will form both $MgCO_3 \cdot 3H_2O$ and $MgCO_3$ on reaction with CO_2. This renders the situation hopeless as far as analysis for percentage composition by any known chemical or thermochemical method is concerned. It has also been shown that MgO, calcined under usual conditions, does not hydrate appreciably when treated with water vapor, and further, that if hydration of MgO does occur in plaster samples, expansion and physical failure do not necessarily result.

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VITA

The author was born in Pittsburgh, Pennsylvania on October 20, 1922. He received his elementary and high school education at Avalon, a suburb of Pittsburgh, graduating from there in 1940. He then entered Washington and Jefferson College, Washington, Pennsylvania, and graduated in September, 1943, with the degree of Bachelor of Science.

From October of 1943 to January of 1946, the author served in the United States Navy. Upon discharge, he worked for the Pittsburgh Testing Laboratory, Pittsburgh, Pennsylvania, doing routine analytical work.

In September of 1946, the author entered the University of Illinois to pursue graduate work toward the Ph. D. degree. During his stay at Illinois, he held a half-time assistantship in analytical chemistry.

The author is a member of Alpha Tau Omega social fraternity and the following honorary societies—Phi Beta Kappa, Phi Kappa Phi, Sigma Xi, Phi Lambda Upsilon, Chi Epsilon Mu, and Phi Chi Mu. He is co-author, with G. L. Clark, of a paper presented at the symposium on the Solid State held at Pittsburgh in June, 1949 and entitled "Observations on the Complexities of the Commonest Solids".

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